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SYNTHESIS OF REFRACTORY COMPOSITES BASED ON CHROMATES OF ALKALINE-EARTH METALS

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Based on model experiments in linear heating of mixtures that are promising refractory compositions, $MCrO_4 + Mg + MgO$ and $MCrO_4 + Al + Al_2O_3$ (M = Mg, Ca, Ba), the temperature conditions of the combustion reactions are determined. All reactions between the components are carried out using solid intra-reaction oxidizers, i.e. chromates of alkaline-earth metals, which are also products of self-propagating high-temperature synthesis. The resulting refractories, with respect to their structural and physicochemical characteristics, are as good as products synthesized using traditional technology.

The majority of refractories are produced on the basis of natural minerals: alumina, dolomite, quartzite, magnesite, etc. In some cases more expensive materials, in particular oxides, are used [1, 2]. Of the two classes of refractory materials (molded and not molded) the first class is more promising for self-propagating high-temperature synthesis (SHS). In earlier studies the synthesis of molded SHS refractories was carried out by preparing an exothermic mixture consisting of chromates of alkaline-earth metals, a reducing material, and a refractory oxide and implementing a process of combustion in special molds in the air atmosphere (international patent applications W 090/05120 dd. 17.05.90 and E 090/13526 dd. 15.11.90). Unfortunately, the practical implementation of this line of research was impeded by the high cost and the absence of substantial industrial volumes of chromates of alkaline-earth metals.

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TABLE 1

System	Open porosity, %	Specific surface area, m²/g	Pycno-metric density, g/cm³	Composition of synthesized products
$MgCrO_4 + Al + Al_2O_3$	3.2	0.4	3.90	$MgAl_2O_4$, $Cr_2O_3 \cdot Al_2O_3$
$CaCrO_4 + Al + Al_2O_3$	3.6	0.6	3.05	$CaAl_2O_4$, $Cr_2O_3 \cdot Al_2O_3$
$BaCrO_4 + Al + Al_2O_3$	3.9	0.4	3.50	$BaAl_2O_4$, $Cr_2O_3 \cdot Al_2O_3$
$MgCrO_4 + Mg + MgO$	3.8	2.0	3.40	$MgO, MgCr_2O_4$
$CaCrO_4 + Mg + MgO$	3.5	0.8	3.60	$CaCr_2O_4, MgO$
$BaCrO_4 + Mg + MgO$	3.8	0.5	4.15	$BaCr_2O_4, MgO$

Therefore, an attempt was made to use alkaline-earth metal chromates previously synthesized by SHS (patent application 96110352/25 dd. 22.05.96) [3, 4] as one of the components of the initial batch for the production of refractory composites (Table 1) and also for model experiments to identify the reaction temperature ranges in refractory composites and determine some of their properties. The experiments were carried out under linear heating at a rate of 10 K/min on a TAG24 S24 SETARAM unit (France) in crucibles made of Al_2O_3. The obtained results show that the process of oxidation of metallic aluminum mainly proceeds within the high-temperature range (900 – 1000°C).

$MgCrO_4 + Al + Al_2O_3$ *system* (Figs. 1 and 2*a*). Virtually all complex chromium-containing oxides of alkaline and alkaline-earth metals are important engineering products. Therefore, it is interesting to investigate the behavior of SHS products under high temperatures. For instance, hydrated magnesium (VI) chromate ($MgCrO_4 \cdot 5H_2O$ or $MgCrO_4 \cdot 7H_2O$) has a great significance in the production of refractories. The SHS product is a crystal hydrate of the $MgCrO_4 \cdot H_2O$ composition that is stable up to a temperature of 250°C. Breaking off of the water molecule occurs within a wide temperature range (250 – 400°C). A stable anhydrous magnesium (VI) chromate belonging to the cubic syngony exists at 400 – 650°C. At a temperature over 700°C, partial dissociation of chromate with a weight loss (12.7%) is observed, which reflects the following simultaneous processes:

$$2MgCrO_4 \rightarrow 2MgO + Cr_2O_3 + 1.5O_2\uparrow;$$

$$MgO + Cr_2O_3 \rightarrow MgCr_2O_4.$$
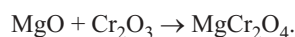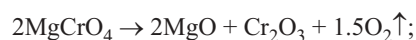
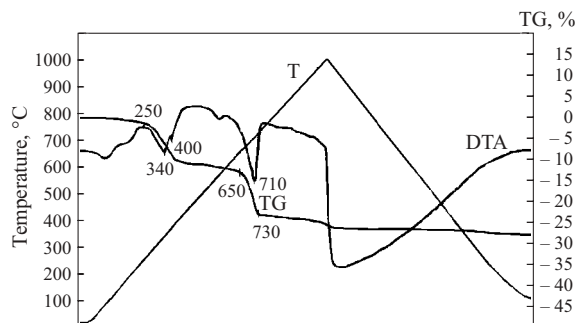The weight loss (12.7% and not 17.1% in removal of $1.5O_2$) is related to a parallel reaction of the formation of the

Fig. 1. Thermogram TG, DTA, and temperature (T) curves in heating $MgCrO_4 \cdot H_2O$.

thermally more stable magnesium chromate in the system. Under a long temperature exposure (750°C), a solid solution $MgO – MgCr_2O_4$ is formed in the system, which is corroborated by the presence of the products of dissolution of magnesium (VI) chromate, i.e., MgO and Cr_2O_3 as well as magnesium chromite in the x-ray pattern.

At a temperature below 650°C the process is similar to the decomposition of hydrated magnesium chromate (Fig. 1), with the only difference that the temperature range in which dehydration takes place is somewhat narrower, i.e., 100 – 350°C instead of 400°C. The temperature of the beginning of thermal dissociation of hydrated magnesium chromate virtually coincides with the melting temperature of metallic aluminum (630 – 650°C). The weight loss in the course of dissociation of magnesium chromate in the presence of metallic aluminum is significantly lower (about 3.89%) that in decomposition of the individual chemical (about 12.7%), which is due to intense oxidation of metal proceeding in two stages with maxima at 920 and 950°C. The oxidation process starts in dissociation of chromate, its temperature heterogeneity is determined by different dispersion of metallic aluminum particles, and its peak at a temperature of 950°C is due to the final oxidation of larger particles.

$CaCrO_4$ + Al + Al_2O_3 system (Fig. 2b). Calcium chromate is thermally more stable than magnesium chromate, therefore, it is not dissociated at a temperature of 1000°C. The complete dehydration of hydrated calcium chromate occurs in two stages in a temperature range of 100 – 300°C with maxima at 120 and 250°C (removal of crystallized water). The endothermic peak with a maximum at 650°C corresponds to metallic aluminum melting. As the temperature increases (approximately starting with 760°C), the aluminum becomes oxidized, first as a consequence of reaction with air oxygen (with a maximum at 890°C) and then as a consequence of calcium chromate melting and decomposing with a maximum at 1020°C (according to the published data, at 1022°C). The oxidation of metallic aluminum is not completed due to a shortage of active intra-reaction oxygen in calcium chromate. This is corroborated by the peak of crystallization of melted aluminum on the cooling curve and its presence in the reaction products.
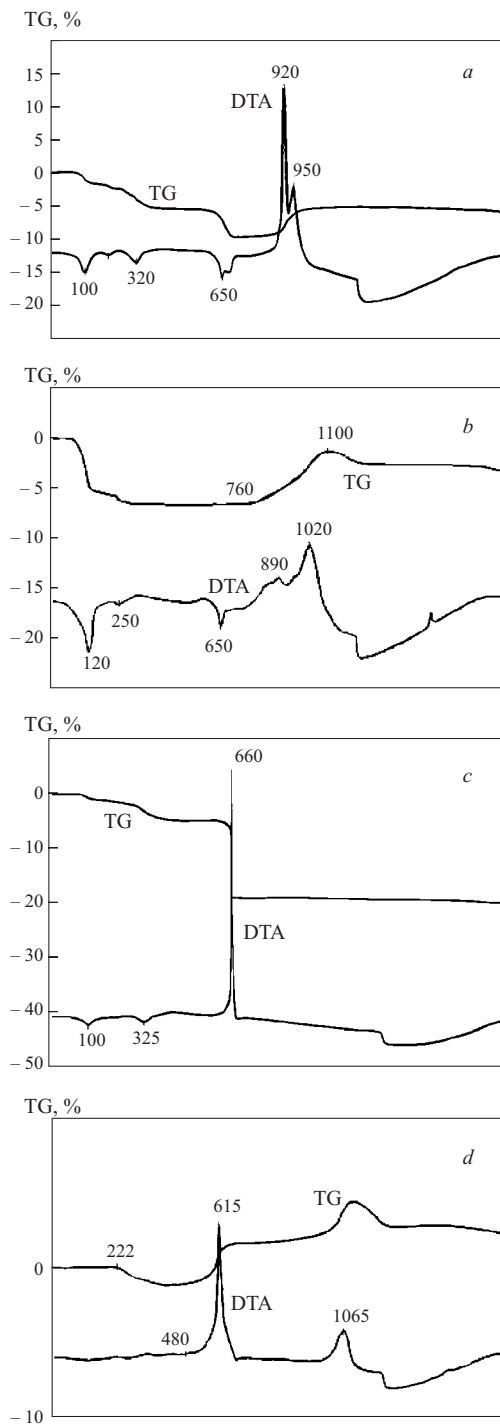
Fig. 2. TG and DTA curves of reactions between the components of mixtures $MgCrO_4 + Al + Al_2O_3$ (a), $CaCrO_4 + Al + Al_2O_3$ (b), $MgCrO_4 + Mg + MgO$ (c), and $CaCrO_4 + Mg + MgO$ (d).

$MgCrO_4$ + Mg + MgO system (Fig. 2c). The reactions between the components in this particular system up to a temperature of 650°C are virtually identical to the process of dehydration of magnesium chromate and its reactions with aluminum and Al_2O_3. This temperature correlates with the melting of metallic magnesium (according to the literature
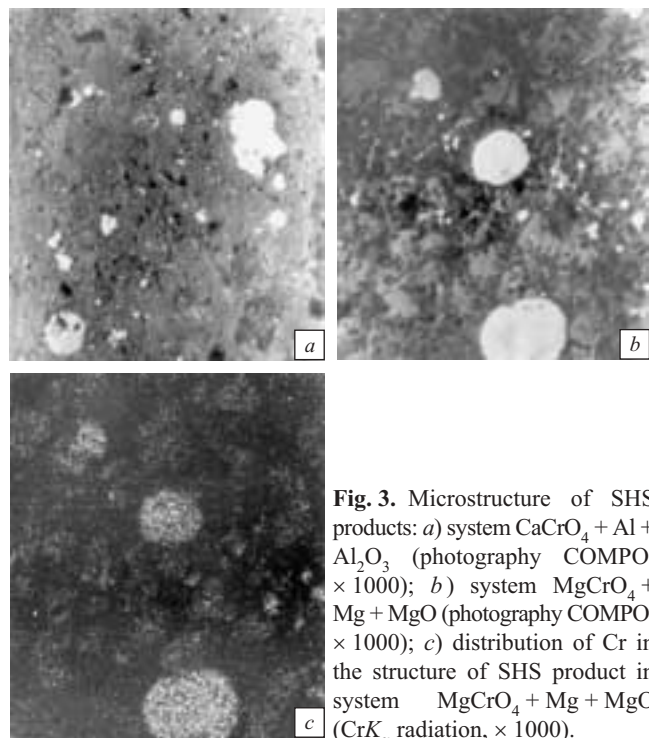
Fig. 3. Microstructure of SHS products: *a*) system $CaCrO_4 + Al + Al_2O_3$ (photography COMPO, × 1000); *b*) system $MgCrO_4 + Mg + MgO$ (photography COMPO, × 1000); *c*) distribution of Cr in the structure of SHS product in system $MgCrO_4 + Mg + MgO$ (CrK_α radiation, × 1000).

data, 651°C). Since magnesium is substantially more active in chemical reactions and in combustion, at a temperature of about 660°C it becomes instantly and intensely exothermically oxidized under heating in the presence of free oxygen released in thermal decomposition of the chromate. This is also indicated by the sample weight loss. The weight loss in decomposition of pure magnesium chromate is equal to about 28%. In the presence of metallic magnesium, the weight loss decreases to 19%, which is evidence of simultaneous very fast thermal desorption oxidation processes. The formation of highly thermostable structures and the completeness of the metallic magnesium reactions is corroborated by the absence of any weight variations and phase transformations at temperatures above 670°C in the stages of heating and cooling of the sample.

$CaCrO_4 + Mg + MgO$ *system* (Fig. 2*d*). Dehydration of calcium chromate (removal of coordination-bonded water) in this system occurs at a temperature over 220°C, as a result of which the system loses about 1.5 wt.%. The oxidation of metallic magnesium in the presence of its oxide and calcium chromate starts at a temperature of about 480°C (with a maximum at 615°C), which is below the temperature of melting of pure metallic magnesium. The weight increment related to the metal oxidation due to air oxygen is about 2.8%, which shows that the process is not completed at temperatures below 1000°C. Thermally stimulated melting of magnesium chromate with subsequent decomposition occurs at temperatures above 1000°C with a maximum at 1065°C and is accompanied by the final oxidation of metallic magnesium to MgO.

It should be noted that the use of chromates of alkaline-earth metals as a material in the production of refractories

makes it possible to exclude preliminary heat treatment from the process, since the water contained in chromates does not has a significant effect in the presence of aluminum an magnesium considering the highly exothermic process. Consequently, hydrated chromates of the type of $CaCrO_4 \cdot 2H_2O$ can also be used as initial materials.

The direct reactions of chromates of alkaline and alkaline-earth metals, which themselves are oxidizers, with metals in combustion resemble the process of combustion of low-gaseous compounds. A positive feature of the material thus obtained is the fact that the refractory material is synthesized as a result of a redox combustion reaction of aluminum, magnesium, or other active materials with oxides. As distinct from standard thermal reducing reactions, in which only some of the reaction products are target products, in the SHS process all products of the batch combustion are target products. They form a densely sintered porous material, which upon being deposited on the surface of bricks, plates, and other products before the combustion process creates a dense protective layer resistant to the effect of high temperatures, aggressive media, etc. [1].

The structure formed in these reactions represents a dense skeleton consisting of spinel phases and individual oxides sintered together, which are the products of decomposition of the respective chromates of alkaline-earth metals and the products of oxidation of metal as a combustible material (Fig. 3). The darker color of the intergrain phase compared with the grain color (COMPO photography) indicated that the mean atomic number of the intergrain phase is smaller than that of the grains. In spite of the fact that in the present study no binder was used in the systems investigated and all combustion processes took place in mechanically mixed dry mixtures, the properties of the combustion products are as good as those of the products of the reactions based on industrially produced chromates of alkaline earth metals (Table 1) [1].

Thus, the considered temperature conditions of reactions and the structural and physicochemical properties of the products of synthesis for promising refractory composites make it possible to describe in detail the mechanism of the combustion reactions and to analyze the properties of refractories that are products of SHS.

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